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Abstract

The experimental procedure to be used to study the effects of electron irradiation on surface properties of germanium and silicon are described. The fabrication procedures for making p-n alloy junctions on n and p Ge and n and p Si of various resistivities are presented. Photovoltaic spectral response and i-V curves of these Si and Ge cells are given and compared to theory.

I. Introduction

Ionizing radiation, i.e. electrons, protons, gamma rays, ultraviolet light etc., are known to cause changes in the surface properties of semiconductors. These effects have not, however, been subjected to any intensive investigation. It is known, for example, that, whenever one is studying the effects of fast electrons which are capable of producing bulk damage in the semiconductor, certain changes which saturate with time may occur during the initial parts of the irradiation.

Early experiments at Brown University (reported at the Fourth Photovoltaic Specialists Conference, Cleveland, Ohio June 1964) showed that silicon solar cells exhibited such "saturable"effects when they were subjected to electrons whose energy was of the order of 100KeV in vacuum. It was further established that the changes if they are to be attributed to surface effects were such that one would conclude that the surface recombination velocity s of an n/p cell decreased while that of a p/n cell increased when the cells were exposed to such radiation. Analysis of the results permitted the setting of limits on the magnitudes of these changes encountered in these cells. It appeared that a change of s by a factor less than 10 was sufficient to account for the observed effects. It was recognized, however, that the commercial solar cell was far from an ideal structure for studying the surface effects of radiation. Such cells are made by diffusing an impurity into a crystal substrate. The surface concentration of the impurity is known only very approximately. Furthermore, it is likely that the characteristics will vary from cell to cell in some uncontrolled way.

In another set of experiments at Brown, this time on germanium, it was found that very large changes (factors of fifty) in the response of photovoltaic cells to short wavelength radiation were observed when a germanium alloy junction photocell was exposed to irradiation by electrons whose energy was too low to produce bulk damage. The effects were reversible in the sense that the response could be cycled between two values established by irradiating the cell until the effect saturated or letting the cell rest in vacuum for a few hours. Such reversible behavior was also observed in the silicon solar cells.

The experiments whose status is described in this preliminary report were undertaken in order to explore this phenomenon, to explain it and perhaps to suggest ways of avoiding the degradation of characteristics observed in some cases and of benefitting from the improvements of characteristics observed in others.

II. Description of the Experiment

A. General

The experimental technique has been described in previous publications and reports. Briefly it involves measuring the short circuit current or parameters proportional to it produced by monochromatic light of selected wavelengths in alloy junctions of germanium and silicon. The light is incident on the surface opposite the junction. The thickness of the semiconductor wafer is approximately one diffusion length L so that carriers generated by strongly absorbed light have a high probability of diffusing across the wafer to the junction where they are collected. Both penetrating and strongly absorbed light should be used. The former serves as a control since the photocurrent produced by weakly absorbed light is proportional to

$$I \sim \alpha L$$

where α is the absorption constant and L is the diffusion length. In the experiments cited above, two or at most three distinct wavelengths were employed. In the experiments currently under way we are using complete spectral response curves, which provide additional information about the behavior of these cells.

The remainder of this report will be devoted to a description of the procedure used in the fabrication of alloy junctions in both n- and p-Ge and Si whose initial resistivities range from a few tenths of an ohm-cm to about fifty ohm-cm; to a discussion of the measured spectral response of these cells and to a description of the apparatus to be used in subsequent portions of this work.

B. Cell Fabrication Procedure

There were four resistivity ranges of n- and p-Ge and four resistivity ranges of n- and p-Si used in the fabrication of alloy junction photovoltaic cells. Table IIB-1 gives details of the properties of these materials as given by the manufacturers. (The germanium crystals were purchased from Sylvania while the silicon crystals were purchased from Texas Instruments.) The material used for forming alloy junctions and for making ohmic contacts to these various materials are listed in Table IIB-2.

Wafers were prepared from Ge and Si ingots by cutting 0.035" slices with a diamond saw. These were then made into pellets of dimensions 0.30" x 0.30"x 0.035". These slices were lapped and polished according to the following procedure. They were first hand lapped on a glass plate with 1000 mesh carborundum and distilled water; about 0.004" was removed from each of the two faces in this lapping operation. After careful cleaning the samples were polished on a wheel in three successive stages with polishing alumina whose particle sizes were 5.0, 0.3 and 0.05µ . An automatic polishing attachment facilitated this stage of pellet preparation. Only one side of the wafer was polished to a mirror surface; this was the surface into which alloying was allowed to proceed. The pellets were now cleaned by boiling successively in trichloroethylene and acetone, rinsing in methanol and finally in deionized double distilled water. The samples were then air dried.

The next step in wafer preparation involved etching. The Ge pellets were etched in CP-4 for 30 seconds, washed in deionized twice distilled water, and then dried in air. The Si pellets were etched in hot NaOH (30% solution) (temperature 100°C) for 5 minutes, washed in deionized distilled water. Another etch (5 parts HNO_3 to 3 parts HF) was also tried. This etch works faster than NaOH but it leaves a surface with well defined etch pits and it was therefore abandoned.

The alloying furnace was designed and constructed at Brown. It consists of a strip of nichrome through which a large (tens of amperes) current is passed. The heated strip (about 1/2" wide, 0.020" thick) is supported between two posts inside a chamber through which hydrogen is allowed to flow. A low power, binocular microscope allows close observation of the alloying process which is terminated when the operator sees the pellet melting. Figure IIB-1 is a schematic diagram of the alloying oven.

The pellets are held in a carbon jig which rests on the nichrome heater. Some pressure must be exerted on the alloy material if good junction formation is desired. The carbon jig has a cover which serves to exert this slight pressure and to homogenize the temperature around the sample. In the case of silicon, the alloy junctions and ohmic contacts are formed simultaneously; this required a higher pressure during alloying process. Figures IIB-2 and IIB-3 show the carbon jigs used for germanium and silicon respectively.

The alloying of indium into n-Ge was accomplished by raising the temperature to 300°C for one minute then heating to 500°C holding the maximum temperature for about 15 seconds. The temperature was then lowered slowly and smoothly for the first 200°C. The junction formation in p-Ge followed this same time cycle but the wetting temperature was set at 450°C and the alloying temperature was 600°C. For both n- and p-Si, the wetting temperature was 600°C and the alloying temperature was 750°C.

The ohmic contacts were made to Ge in a second step. A Kovar ring was the base for the contact. It was covered with solder, the Ge wafer with p-n junction was placed in contact with the solder covered Kovar ring and the structure was heated to 300°C for 30 seconds.

The finished Ge cells were then subjected to a final etch in CP-4 (30 seconds) while the Si cells were etched in a solution containing HNO_3, HF and CH_3OOH in the ratio 5:3:1.

The i-V characteristics of the cells were examined with the help of a Tektronix 575 Curve Tracer. Usually four cells were made on each resistivity type, but four good cells did not always result. It is difficult to establish what parameters were at fault in the cells which exhibited inferior i-V characteristics and photovoltaic characteristics.

Table IIB-1 Starting material for fabrication of Photovoltaic cells.

1) <u>N-Ge</u> Zone levelled, Sb-doped, (111)direction

0.11-0.14 ohm-cm	:	dislocation density	500-1,100 pits/cm^2
		lifetime	-
1.10-1.30 ohm-cm	:	dislocation density	400-900 pits/cm^2
		lifetime	30 μ sec
6.2-9.0 ohm-cm	:	dislocation density	900-1,400 pits/cm^2
		lifetime	90 μ sec
22.0-30.0 ohm-cm	:	dislocation density	700-1,400 pits/cm^2
		lifetime	200 μsec

2) <u>P-Ge</u> Zone levelled, (111) direction

0.11-0.15 ohm-cm	:	In-doped	
		dislocation density	500-1,800 pits/cm^2
		lifetime	-
1.10-1.50 ohm-cm	:	In-doped	
		dislocation density	700-1,200 pits/cm^2
		lifetime	30 μ sec
9.0-10.5 ohm-cm	:	Ga-doped	
		dislocation density	400-900 pits/cm^2
		lifetime	90 μ sec
28.0-40.0 ohm-cm	:	Ga-doped	
		dislocation density	2,000-3,700 pits/cm^2
		lifetime	200 μ sec

3) <u>N-Si</u> Floating zone, (111) direction, P-doped

0.075-0.125 ohm-cm

0.75-1.25 ohm-cm

7.5-12.5 ohm-cm

38-62 ohm-cm

4) <u>P-Si</u> Floating zone, (111) direction, B-doped

0.07-0.13 ohm-cm

0.75-1.25 ohm-cm

7.5-13 ohm-cm

38-62 ohm-cm

Table IIB-2 Alloying and Ohmic Contact Materials

<u>Alloy Junction Materials</u> (disc dia. :0.125"φx 0.010" th.)

a) Pure In discs (for N-Ge)

b) 90% Pb + 10% Sb discs (for P-Ge)

c) 89% Al + 11% Si discs (for N-Si)

d) 99.5% Au + 0.5% Sb Discs (for P-Si)

<u>Ohmic Contacts Materials</u>

1. Kovar rings---Electrode

   0.350" O.D. x 0.234 I.D. x 0.010 thick

2. Solders (dia.: 0.08" x 0.04" x 0.01" th.)

   a) 97% Sn + 3% Sb (for N-Ge)

   b) 90% Pb + 10% Sn (for P-Ge)

   c) 99.5% Au + 0.5% Sb (for N-Si)

   d) 89% Al + 11% Si (for P-Si)

3. Flux---$ZnCl_2$ solution (for Ge)

(Note)
Alloy junction & ohmic contacts materials were cleaned as follows:

(1) Boil in trichlorethylene

(2) Boil in acetone

(3) Rinse in methanol (2 times)

(4) Rinse in double distilled water (3 times)

(5) Dry on a filter paper and under an infrared lamp

(6) Etch in HCl for 1 minute

(7) Rinse in distilled water (3 times)

(8) Dry on a filter paper and under an infrared lamp

Figure Titles; Section IIB

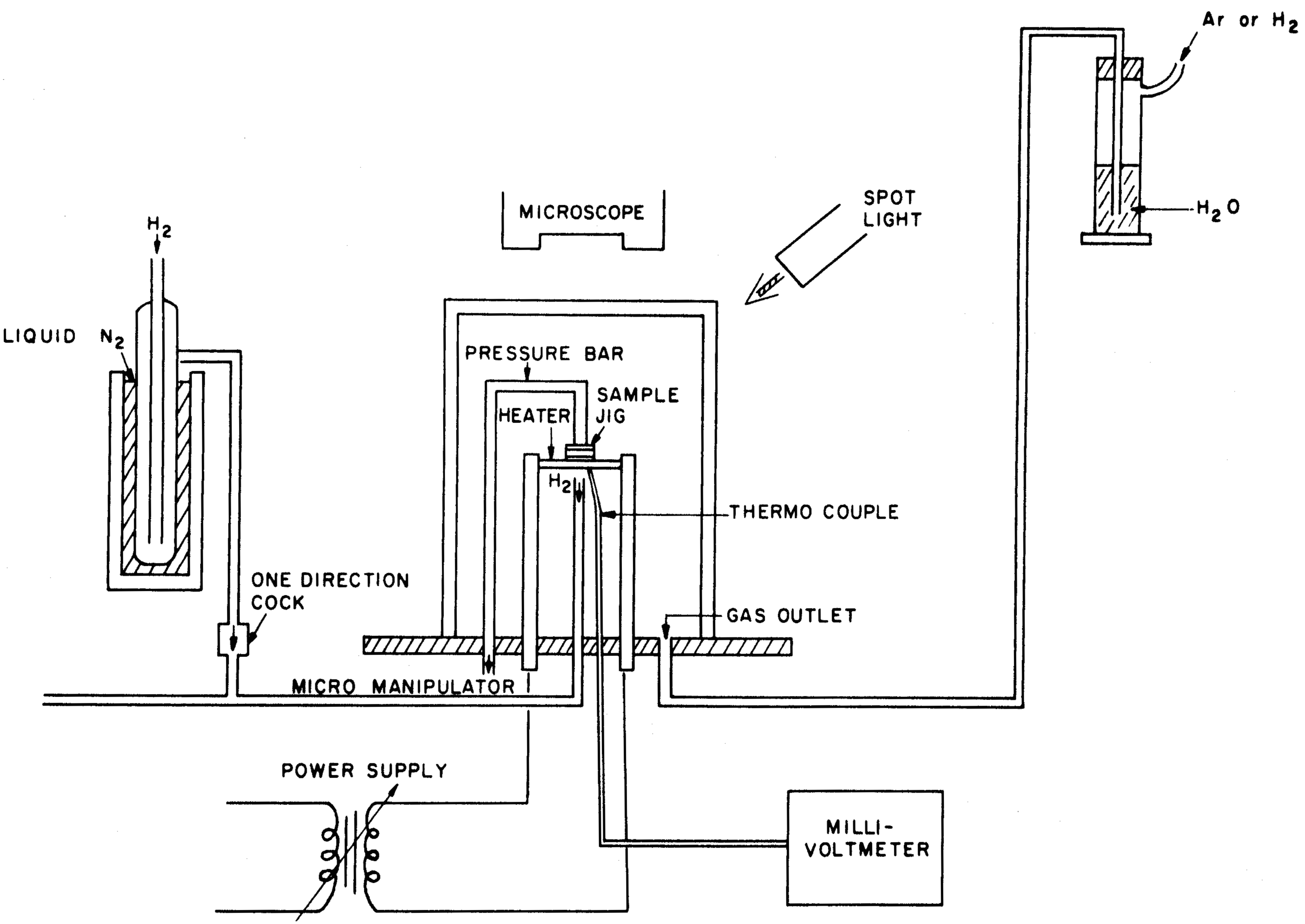


FIG. II B-1 SCHEMATIC DIAGRAM OF ALLOYING EQUIPMENT

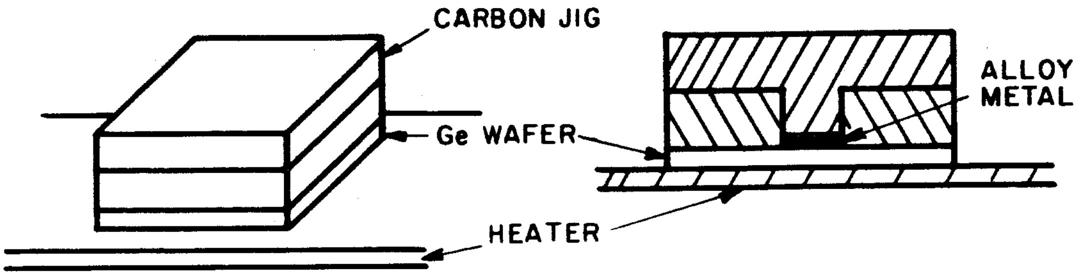


FIG. II B-2 JIG FOR ALLOYING Ge CELLS

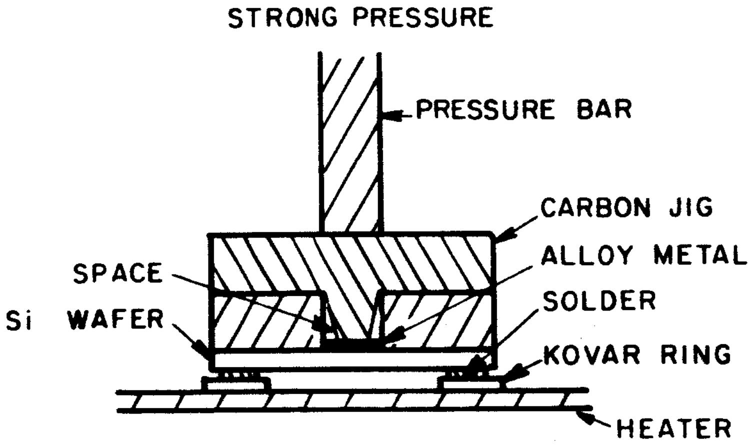


FIG. II B-3 JIG FOR ALLOYING Si CELLS

C. Measurement of Spectral Response and i-V Characteristics Before Irradiation

The source of monochromatic light was a Bausch and Lomb grating monochromator fitted with filters to isolate the desired order. Both ac and dc measurements were made. The ac response of the cell was measured by a Hewlett-Packard A. C. Millivoltimeter while the dc response was measured by a Keithley Microvoltmeter. The slit width of the monochromator was adjusted for each cell to such a value that the maximum cell output did not exceed about 1 mV. If the output voltage is maintained at such a low value, the open circuit voltage remains proportional to the short circuit current V_{oc} of the cell. (In general,

$$V_{oc} = \frac{kT}{e} \ln \left(\frac{Is}{Io} + 1\right)$$

where I_s is the light-generated short circuit current and I_o is the reverse current of the junction. If

$$\frac{I_s}{I_o} << 1,$$

then

$$V_{oc} = \frac{kT}{e} \quad \frac{Is}{I_o} \quad .$$

Since $$\frac{kT}{e} \sim 0.025V \text{ at } 300°K,$$

the condition $I_s/I_o < 1$ reduces to the requirement that $V_{oc} << 0.025V$. A value of 1 mV was chosen as the upper bound on V_{oc} to assure that this condition be met.)

A sketch of the experimental arrangement is shown in Figure IIC-1. The frequency of the modulated light was a few hundred cps.; it was kept within the range where the response was independent of frequency. Figure IIC-2 shows the spectral response for n-Ge of various resistivities and Figure IIC-3 shows the same sort of data for p-Ge. These curves also show α vs λ. The penetration of the light can be taken to be inversely proportional to α.

Figure IIC-4 shows the photovoltaic current-voltage characteristics of p- and n-Ge cells exposed to both penetrating (1.82 microns) and strongly absorbed (1.05 microns) light. The i-V curves were independent of λ .

Figure IIC-5 represents the spectral response of n- and p-Si cells of various resistivities while Figure IIC-6 shows the i-V characteristics of these same cells exposed to either penetrating (1.15 microns) or strongly absorbed (1.00 micron) light.

The i-V characteristic is recorded by connecting a variable resistance across the illuminated cell and measuring i_L and V_L as the resistance is varied. The equation obeyed by these curves (for an ideal diode) is of course,

$$i_L = i_s - \left(\frac{e\, i_o}{kT}\right) V$$

Their slope yields $\frac{e\, i_o}{kT}$ and one can therefore compute i_o. The values of i_o computed from these curves are given in Tables IIC-1 (Ge) and IIC-2 (Si).

D. Discussion of Photovoltaic Characteristics of the Cells.

As we have already pointed out, the short wavelength response should be very sensitive to both the surface recombination velocity and to the diffusion length of the cells. This dependence on diffusion length should be in accordance with the relation

$$i \;\alpha\; e^{-\alpha L}$$

Since minority carrier lifetime τ and therefore diffusion length L are larger in higher resistivity material (as explained by the Hall, Shockley-Reed theory of recombination at a single level) it is reasonable to expect that high ρ -Ge should have a proportionately greater short wavelength response. This is borne out by the measurements on both n and p material (Fig. IIC-2 and IIC-3). The short wavelength response of all these Ge cells is sufficient to insure easy observation of changes in surface recombination velocity. As for i_o the values of i_o should be directly proportional to the resistivity if the surface plays no role in determining i_o. Table IIC-1 shows that while i_o increases with ρ in p-Ge it is certainly not proportional to ρ . In n-Ge the lack of proportionality is even more evident. However, in both cases the values of i_o are similar to those customarily encountered in commercial cells of comparable dimensions.

As for the Si cells, Figure IIC-5 shows that they have very little response in the short wavelength region.This implies that either L is too low in the starting material or else the surface recombination velocity of the finished cells is too high. The values of i_o given in Table IIC-2 are lower than those given for Ge in Table IIC-1 as indeed they should be since i_o is also proportional to n_i^2 where n_i is the carrier concentration in intrinsic material. Some of these values of i_o are again comparable to average commercial junctions of similar dimensions. One of the most striking differences between Si and Ge is the much wider range of value of i_o encountered in Si cells fabricated under what were essentially identical conditions. The photovoltaic output of the Si cells also reflected a large range (factors of more than 100) in the open circuit voltage of cells made on wafers cut from the same Si ingot. The reasons for this variability are presently under investigation. If they are attributable to the value of s on the side opposite the junction, irradiation may stabilize the surface at some higher value than that achieved by present etching techniques.

Table IIC-1 Measured Slopes of i-V Characteristics and Computed Values of i_o for the Germanium Cells

Samples		λ=1.05μ		λ=1.82μ	
		Slope (Ω^{-1})	I_o(μA)	Slope(Ω^{-1})	I_o(μA)
n-Ge	"1"	0.234×10^3	107.0	0.217×10^3	115.0
23-30 Ωcm	"2"	0.210×10^3	119.0	0.189×10^3	132.0
n-Ge	"1"	0.30×10^3	83.0	0.333×10^3	76.0
6.2-9.0	"2"	0.21×10^3	119.0	0.230×10^3	109.0
n-Ge	"1"	0.455×10^3	55.0	0.465×10^3	54.0
1.1-1.3 Ωcm	"2"	0.363×10^3	69.0	0.393×10^3	63.0
n-Ge	"1"	-	-	1.82×10^3	13.7
0.11-0.15Ωcm	"2"				
p-Ge	"1"	0.233×10^3	107.0	0.298×10^3	84.0
28-40 Ωcm	"2"	0.32×10^3	78.0	0.370×10^3	67.0
p-Ge	"1"	0.426×10^3	59.0	0.500×10^3	50.0
9.0-10.5 Ωcm	"2"	0.416×10^3	60.0	0.500×10^3	50.0
p-Ge	"1"	2.56×10^3	9.70	3.26×10^3	7.70
1.1-1.5 Ωcm	"2"	2.57×10^3	9.70	3.35×10^3	7.80
p-Ge	"1"	7.1×10^3	3.50	5.6×10^3	4.48
0.11-0.15Ω cm	"2"	10.1×10^3	2.48	8.6×10^3	2.91

Table IIC-2 Measured Slopes of i-V Characteristics and Computed Values of i_o for the Silicon Cells

Samples		Slope	$I_o(\mu A)$	Samples		Slope	$I_o(\mu A)$
n-Si(0.075-0.125 Ωcm)		20.0×10^3	1.25	p-Si	1	7.7×10^3	3.25
				0.75-1.25 Ωcm	2	500.0×10^3	0.05
	1	6.4×10^3	3.90				
n-Si	2	2.20×10^3	1.14				
0.75-1.25 Ωcm	3	91.0×10^3	0.28	p-Si	1	910.0×10^3	0.027
				7.0-13 Ωcm	2	1600.0×10^3	0.015
n-Si	1	11.8×10^3	2.15				
7.5-12.5 Ωcm	2	14.5×10^3	1.72		1	400.0×10^3	0.062
	3	59.0×10^3	0.42	p-Si	2	31.0×10^3	0.81
				38-62 Ωcm	3	4.8×10^3	5.20
					4	330.0×10^3	0.076
	1	54.0×10^3	0.46				
n-Si	2	77.0×10^3	0.32				
38-67 Ωcm	3	187.0×10^3	0.14				
	4	335.0×10^3	0.07				
	1	3.56×10^3	7.00				
n-Si	2	8.0×10^3	3.10				
7.5-12.5 Ωcm	3	500.0×10^3	0.05				
(RCA)	4	4.8×10^3	5.20				

Figure Titles: Section IIC

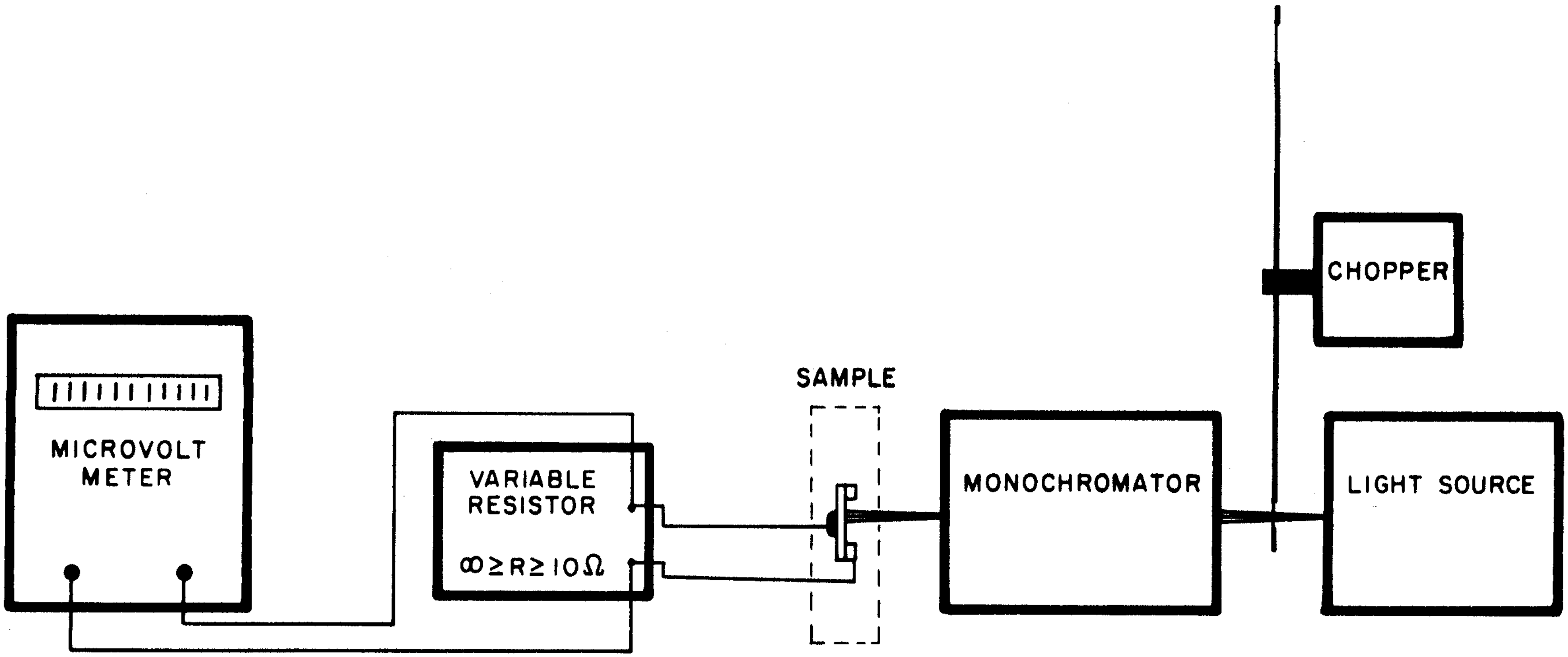
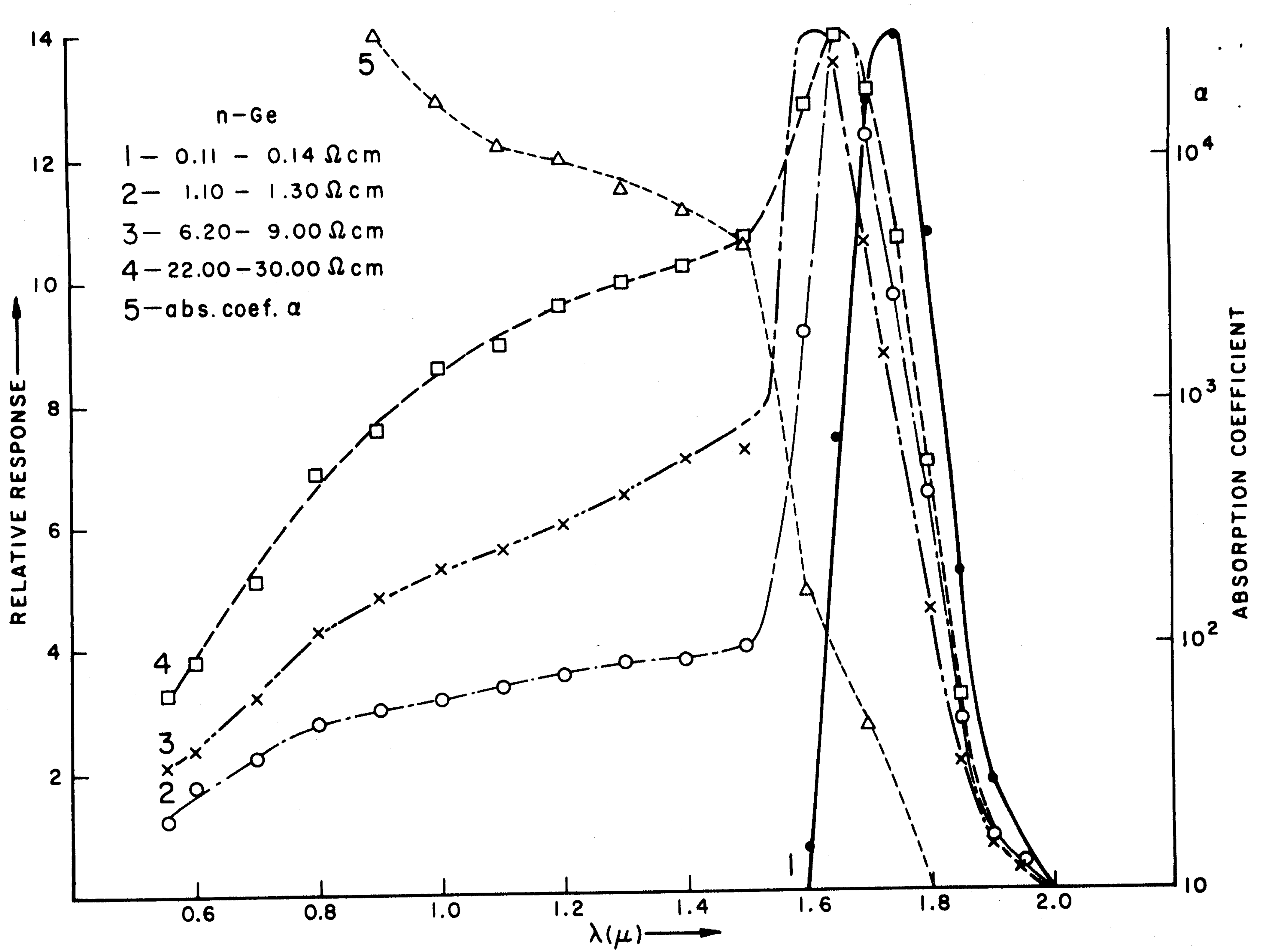

CHOPPER
SAMPLE
MICROVOLT
METER
VARIABLE
RESISTOR
$\infty \geq R \geq 10\Omega$
MONOCHROMATOR
LIGHT SOURCE

FIG. II C-1



n-Ge
1 — 0.11 – 0.14 Ωcm
2 — 1.10 – 1.30 Ωcm
3 — 6.20 – 9.00 Ωcm
4 — 22.00 – 30.00 Ωcm
5 — abs. coef. α
RELATIVE RESPONSE
ABSORPTION COEFFICIENT
α
λ(μ)
14
12
10
8
6
4
2
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
10
10^2
10^3
10^4
1
2
3
4
5

FIG. II C-2

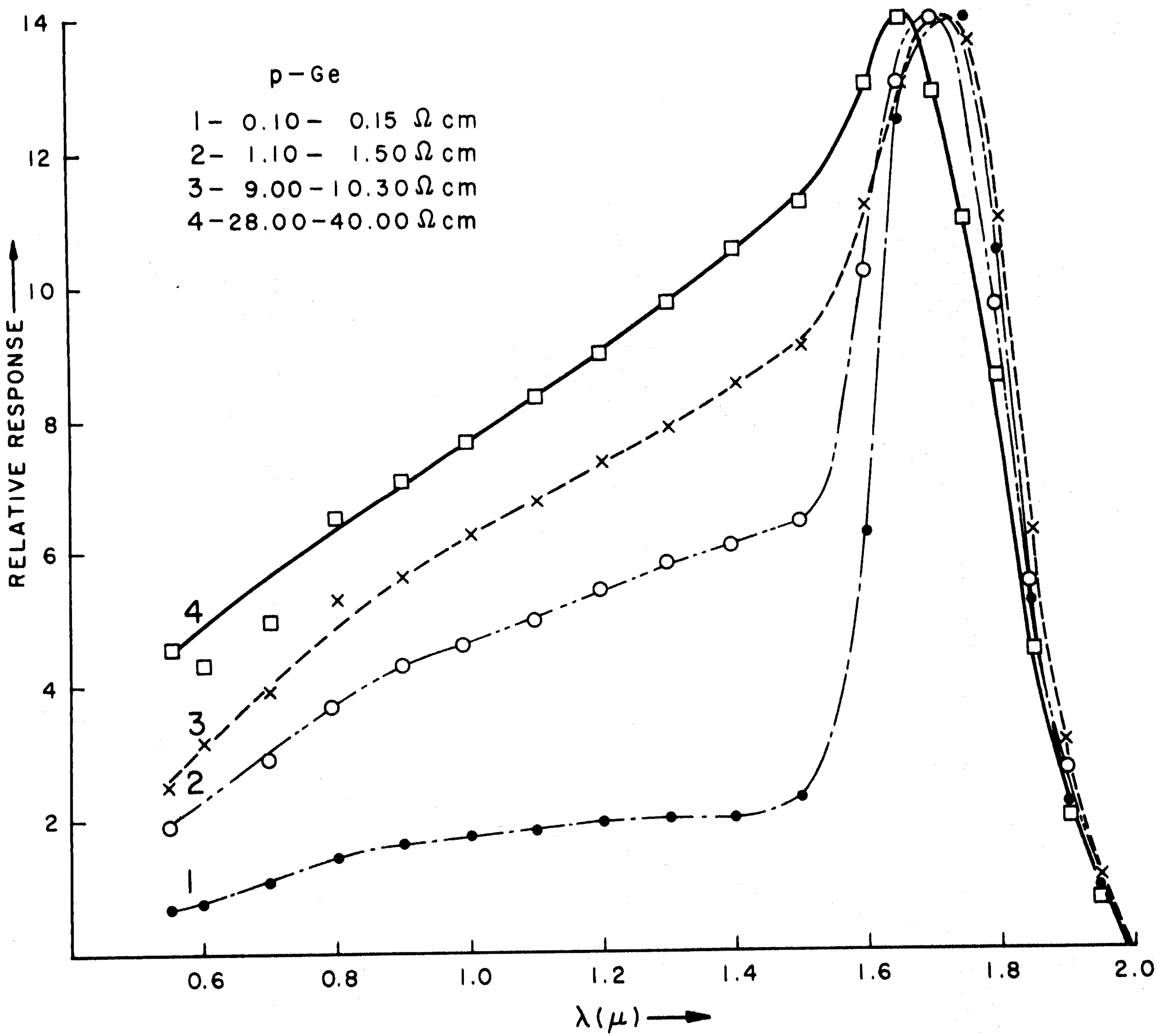
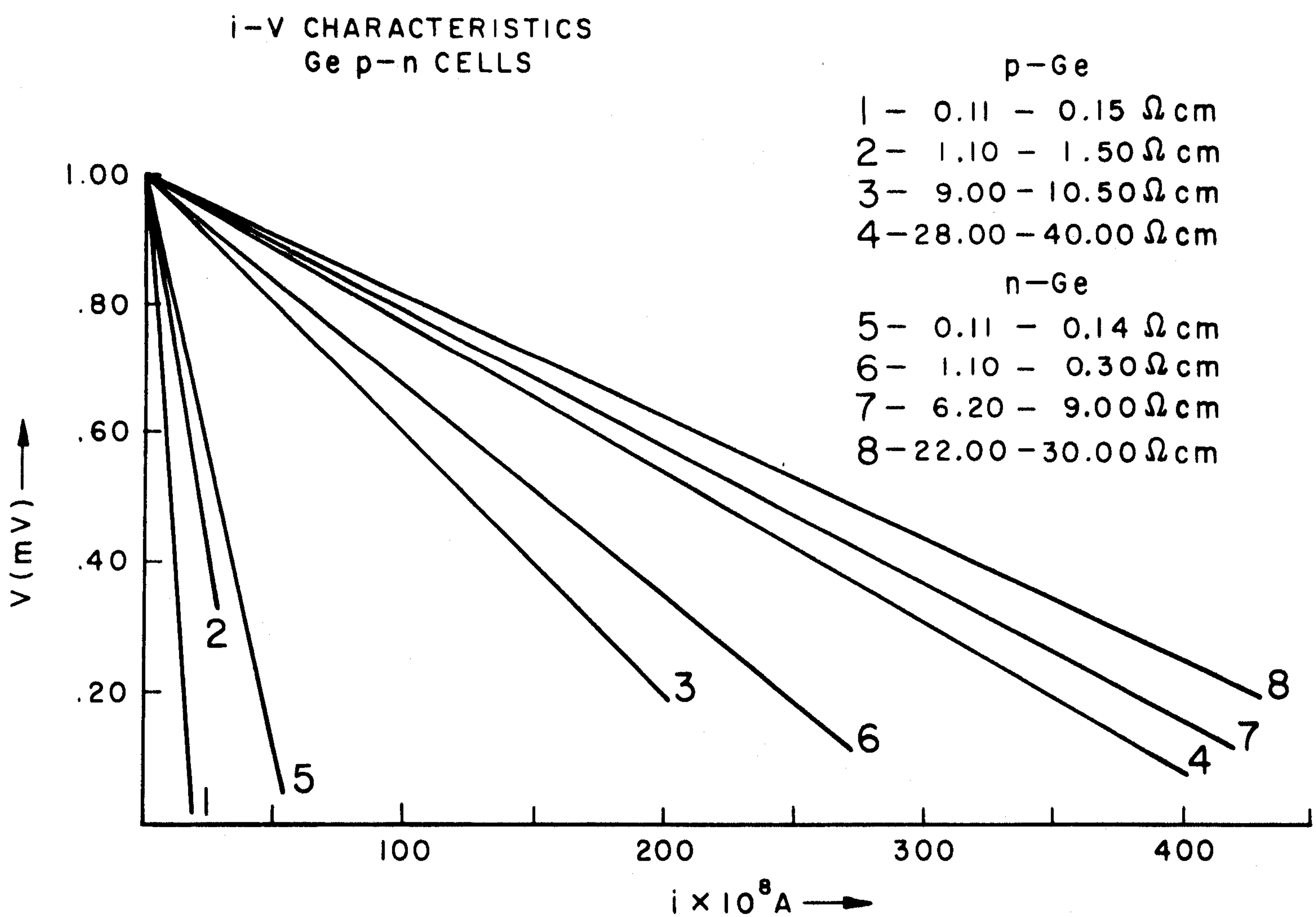
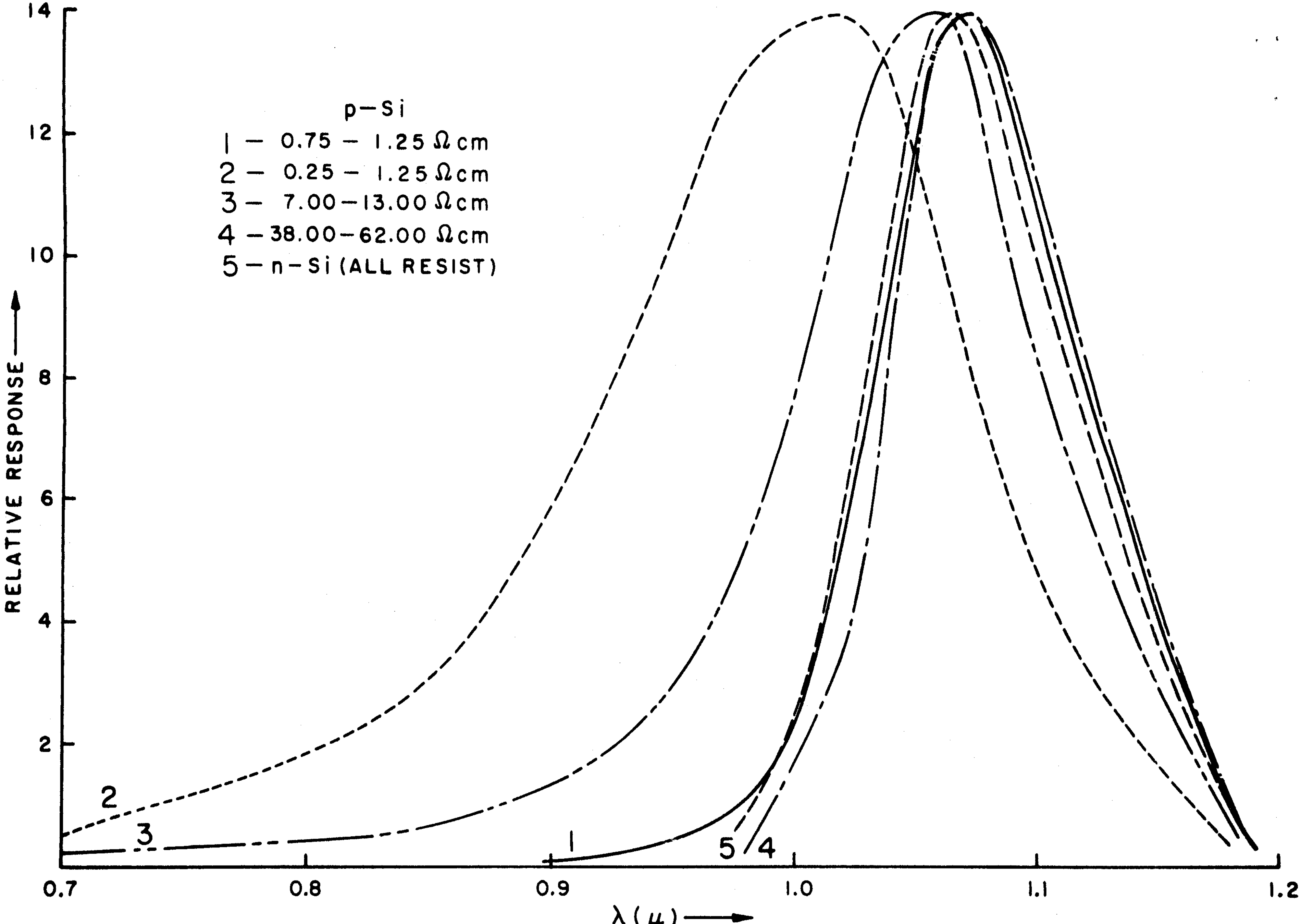

p − Ge
1 − 0.10 − 0.15 Ω cm
2 − 1.10 − 1.50 Ω cm
3 − 9.00 − 10.30 Ω cm
4 − 28.00 − 40.00 Ω cm
RELATIVE RESPONSE
λ(μ)
1
2
3
4
14
12
10
8
6
4
2
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0

FIG. II C-3



i–V CHARACTERISTICS
Ge p–n CELLS
p–Ge
1 – 0.11 – 0.15 Ωcm
2 – 1.10 – 1.50 Ωcm
3 – 9.00 – 10.50 Ωcm
4 – 28.00 – 40.00 Ωcm
n–Ge
5 – 0.11 – 0.14 Ωcm
6 – 1.10 – 0.30 Ωcm
7 – 6.20 – 9.00 Ωcm
8 – 22.00 – 30.00 Ωcm
1.00
.80
.60
.40
.20
V (mV)
100
200
300
400
i × 10^8 A
1
2
3
4
5
6
7
8

FIG. II C–4



p—Si
1 — 0.75 — 1.25 Ωcm
2 — 0.25 — 1.25 Ωcm
3 — 7.00—13.00 Ωcm
4 —38.00—62.00 Ωcm
5 — n-Si (ALL RESIST)
RELATIVE RESPONSE
λ (μ)
14
12
10
8
6
4
2
0.7
0.8
0.9
1.0
1.1
1.2
1
2
3
4
5

FIG. II C-5

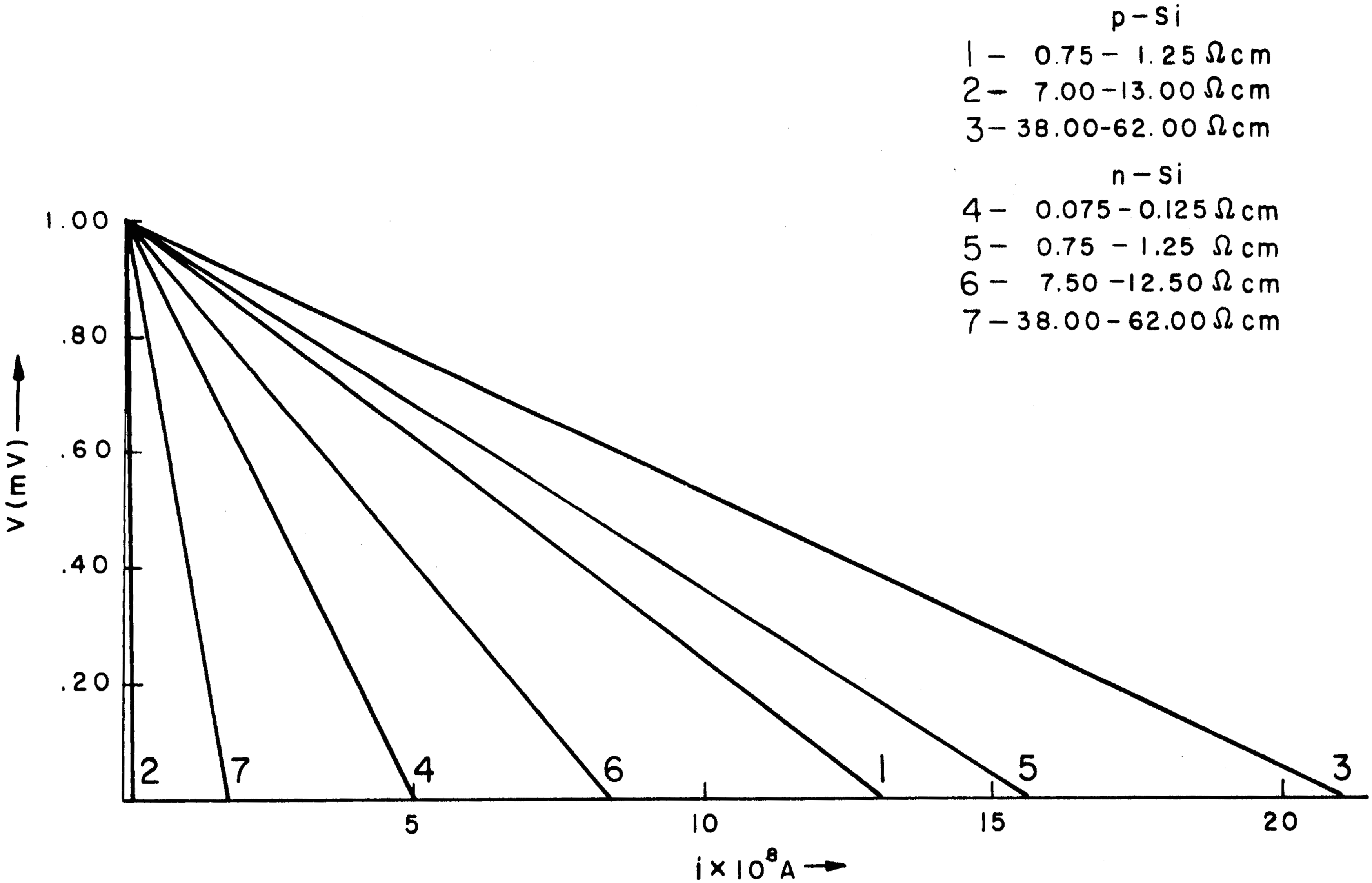

p-Si
1- 0.75- 1.25 Ωcm
2- 7.00-13.00 Ωcm
3-38.00-62.00 Ωcm
n-Si
4- 0.075-0.125 Ωcm
5- 0.75 - 1.25 Ωcm
6- 7.50 -12.50 Ωcm
7-38.00-62.00 Ωcm
1.00
.80
.60
.40
.20
V(mV)
2
7
4
6
1
5
3
5
10
15
20
i×10⁸A

FIG. II C-6

E. Apparatus for Irradiation of Cells by Electrons

In our earlier experiments on Si solar cells and on Ge alloy junction cells, attempts were made to keep the vacuum chamber in which the surface encountered the electrons free from organic vapors. In the case of Si, this was accomplished by separating the irradiation chamber from the machine vacuum by a 0.001" Al window. The irradiation chamber was evacuated by a separate oil diffusion pump fitted with a liquid nitrogen coldtrap. Our concern with organic vapors stems from the fact that electrons interact with such vapors, "crack" them, and cause deposition of carbon on the irradiated surfaces. Such deposits could affect s. Our goal in this program is to study the effect of radiation on the semiconductor surface independent of interference from such organic contaminants. Consequently, the first irradiation experiments will be performed in a glass chamber evacuated by sorption pumps and a Vac-Ion pumping system. The irradiation chamber is separated from the machine vacuum by the 0.001" window as before. The pumping system has been tested and is functioning. The samples will be kept at constant temperature by water cooling. At least five cells will be irradiated simultaneously. Sample holders are presently being assembled.

III. Conclusions

1. About 24 Si alloy junctions have been fabricated on wafers of various resistivities. About 16 Ge alloy junctions have also been fabricated.

2. Preliminary photovoltaic spectral response and i-V curves have been constructed for all of these cells. The i-V curves behave generally as predicted; the computed i_o values could be lower. The spectral response curves of the Ge diodes show substantial short wavelength response whereas the response of Si cells is confined to a narrow spectral region around the absorption edge.

3. Apparatus for irradiation has been designed and is presently being assembled.